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(54) **PROCESS FOR HEAVY OIL UPGRADING IN A DOUBLE-WALL REACTOR**

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B01J 19/24 (2006.01)
C10G 9/40 (2006.01)

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(58) **Field of Classification Search**
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(Continued)

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,818,371 A	4/1989	Bain et al.	
4,840,725 A	6/1989	Paspek	

(Continued)

FOREIGN PATENT DOCUMENTS

FR	3001156 A1	7/2014	
WO	2014032669 A1	3/2014	
WO	2014032671 A1	3/2014	

OTHER PUBLICATIONS

Calzavara et al., "A new reactor concept for hydrothermal oxidation", Journal of Supercritical Fluids, 2004, pp. 195-206, vol. 31, Elsevier.

(Continued)

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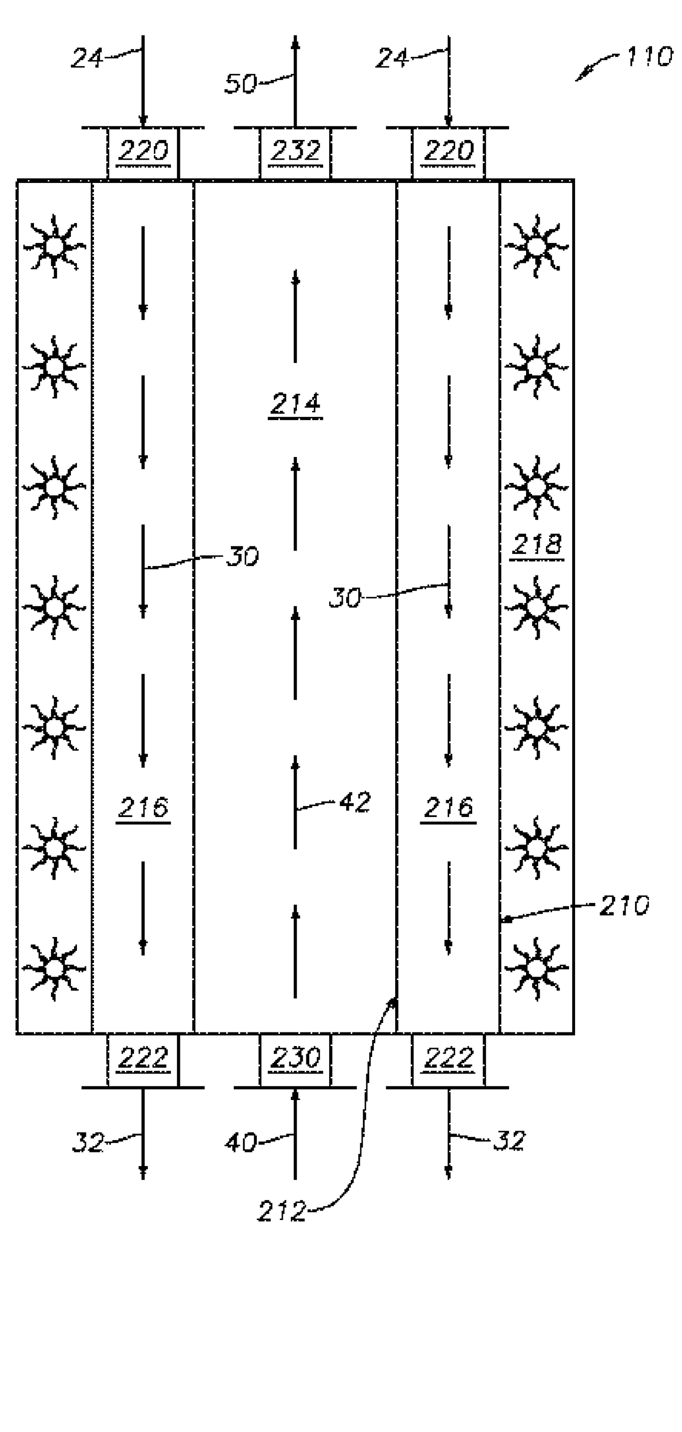
(57) **ABSTRACT**

A process for reducing coke formation during hydrocarbon upgrading reactions using a double-wall reactor comprising the steps of feeding a heated feed water to a shell-side volume of the double-wall reactor to produce a heat transfer stream, the double-wall reactor comprising an exterior wall and an interior wall, a reaction section volume, a heating element configured to heat the heat transfer stream, wherein heat is transferred from the heat transfer stream to the reaction section volume, feeding the hot water return exiting the shell-side volume through a filter; mixing the filtered water stream with a heated hydrocarbon feedstock; feeding the mixed stream to the reaction section volume in a configuration counter-current to the heat transfer stream; reacting the reaction flow stream at a reaction temperature, wherein the heat transferred to the reaction section volume is operable to maintain the reaction temperature above the critical temperature of water.

10 Claims, 7 Drawing Sheets



(52) **U.S. Cl.**
CPC *B01J 2219/00105* (2013.01); *B01J 2219/00135* (2013.01); *B01J 2219/00157* (2013.01); *B01J 2219/24* (2013.01); *C10G 2300/708* (2013.01)

(58) **Field of Classification Search**
CPC B01J 20/28045; B01J 20/28066; B01J 20/28073; B01J 20/28076; B01J 20/3057; B01J 20/3078; B01J 20/3204; B01J 20/3214; B01J 2219/00094; B01J 2219/00105; B01J 2219/0011; B01J 2219/00135; B01J 2219/00157; B01J 2219/00159; B01J 3/008; C10G 1/002; C10G 1/065; C10G 2300/202; C10G 2300/206; C10G 2300/708; C10G 31/08; C10G 45/26; C10G 49/18; C10G 55/04; C10G 9/40; G05D 1/027; G05D 1/0274; G05D 1/0278; G05D 2201/0201
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,900,429	A	2/1990	Richardson
5,008,085	A	4/1991	Bain et al.
5,356,530	A	10/1994	Calderon
5,358,646	A	10/1994	Gloyna et al.
5,554,347	A	9/1996	Busson et al.
6,312,652	B1	11/2001	Duncan
6,485,631	B1	11/2002	Ellingsen
6,749,816	B1	6/2004	Hasegawa et al.
7,255,372	B2	8/2007	Bertholin et al.
7,591,983	B2	9/2009	Takahashi et al.
8,196,658	B2	6/2012	Miller et al.
8,197,670	B2	6/2012	Li et al.
8,349,268	B2	1/2013	Yeung
8,636,323	B2	1/2014	Prince-Wright et al.
2004/0232046	A1	11/2004	Tanaka et al.
2008/0099378	A1	5/2008	He et al.
2009/0206007	A1	8/2009	Allam
2010/0189610	A1	7/2010	Allam
2012/0061291	A1	3/2012	Choi et al.
2012/0149944	A1	6/2012	Zmierczak et al.
2014/0099691	A1	4/2014	Iversen
2014/0109465	A1	4/2014	Coppola et al.

OTHER PUBLICATIONS

International Search Report and Written Opinion for related PCT application PCT/US2015/061536 dated Apr. 6, 2016.

Vilcaez et al., "Hydrothermal extractive upgrading of bitumen without coke formation", Fuel, 2012, pp. 379-385, vol. 102, Elsevier.

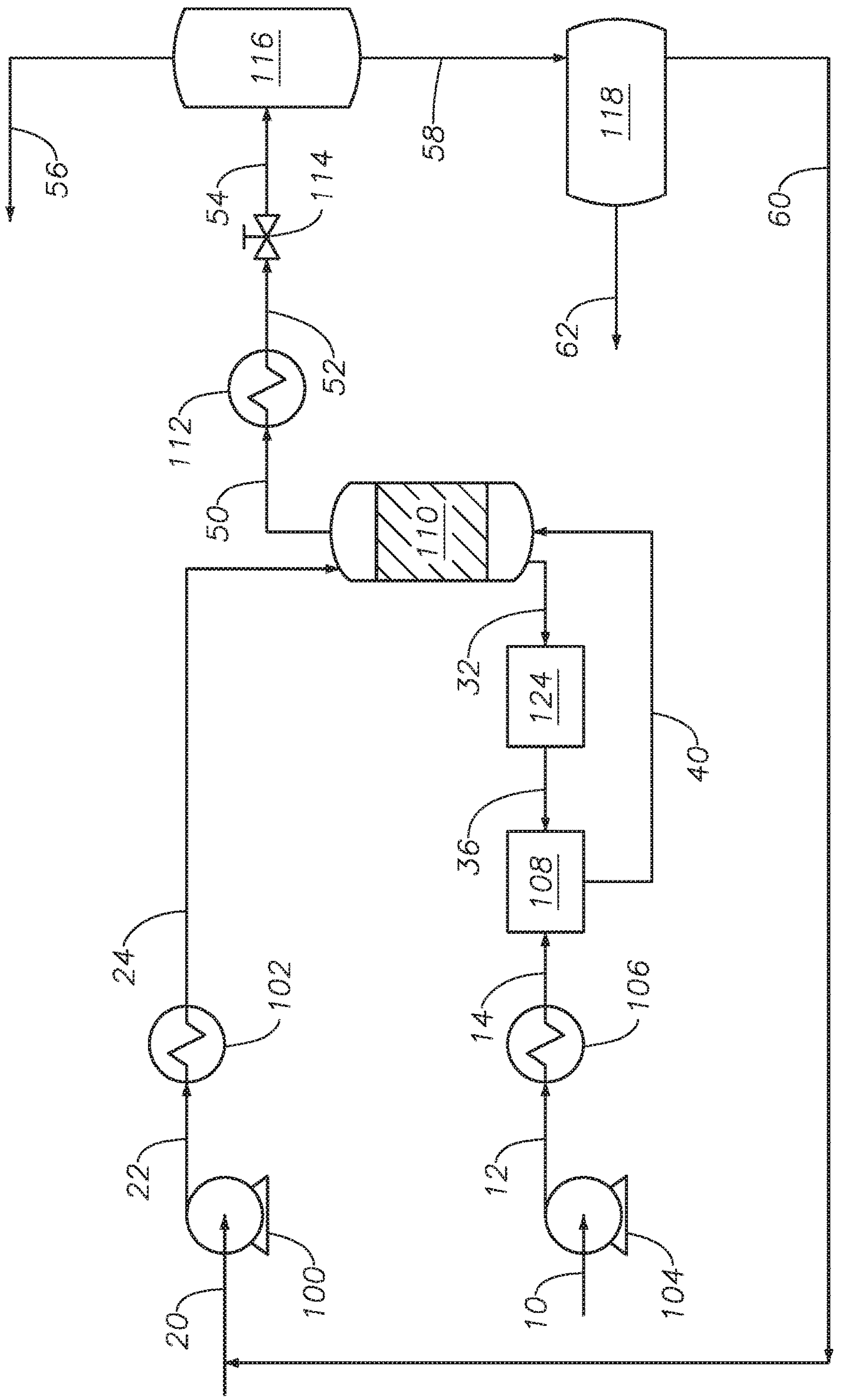

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FIG. 1

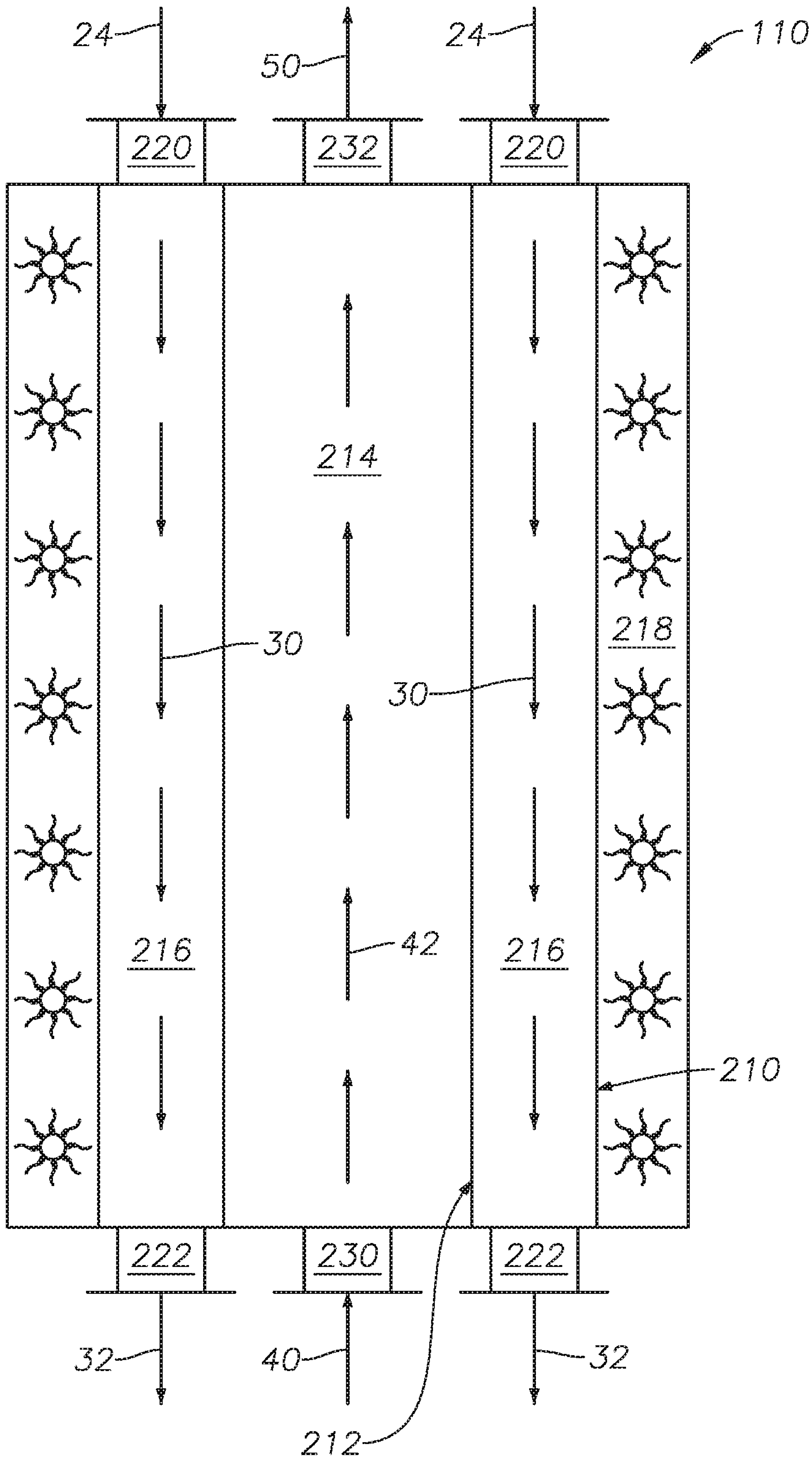
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FIG. 2

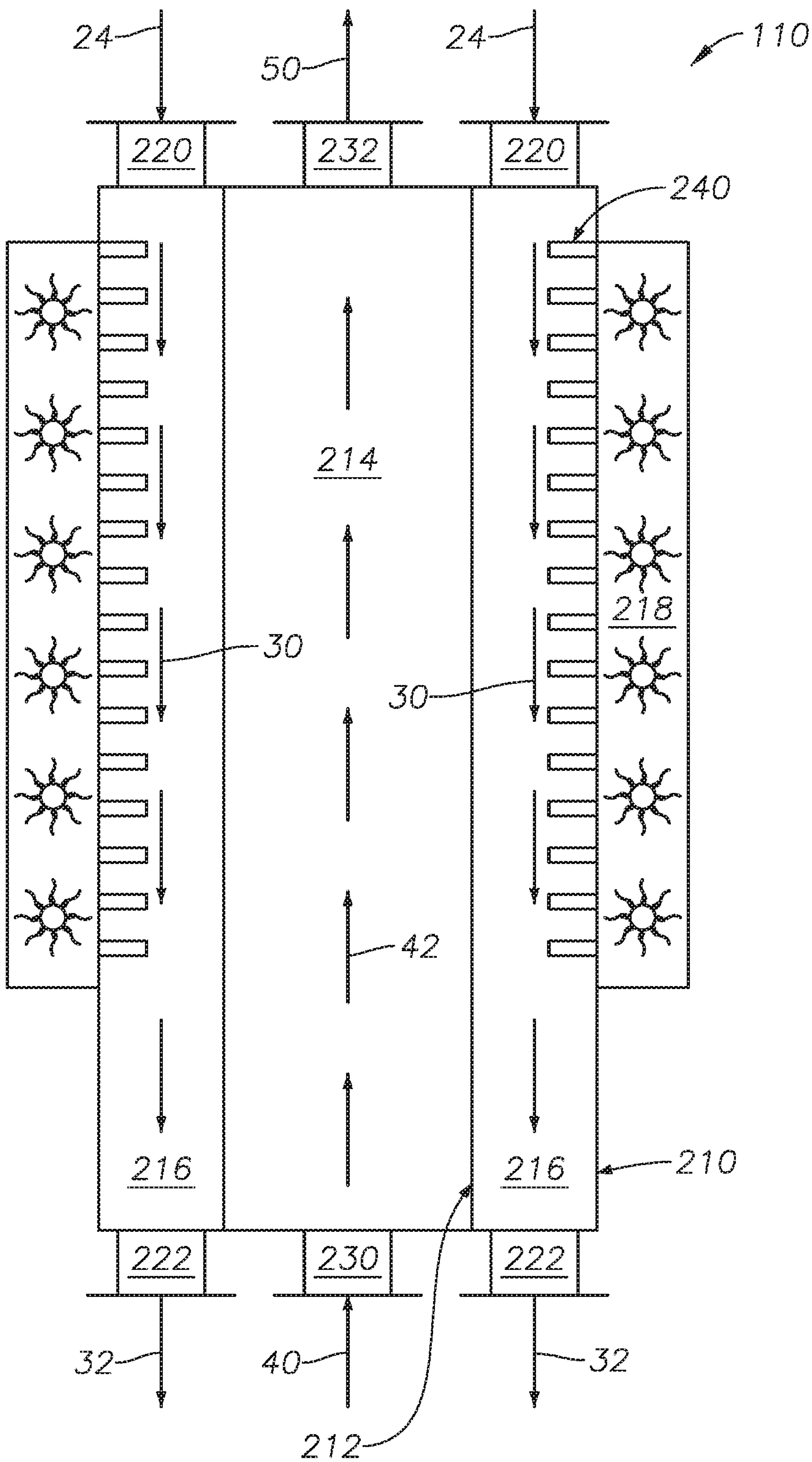

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FIG. 2a

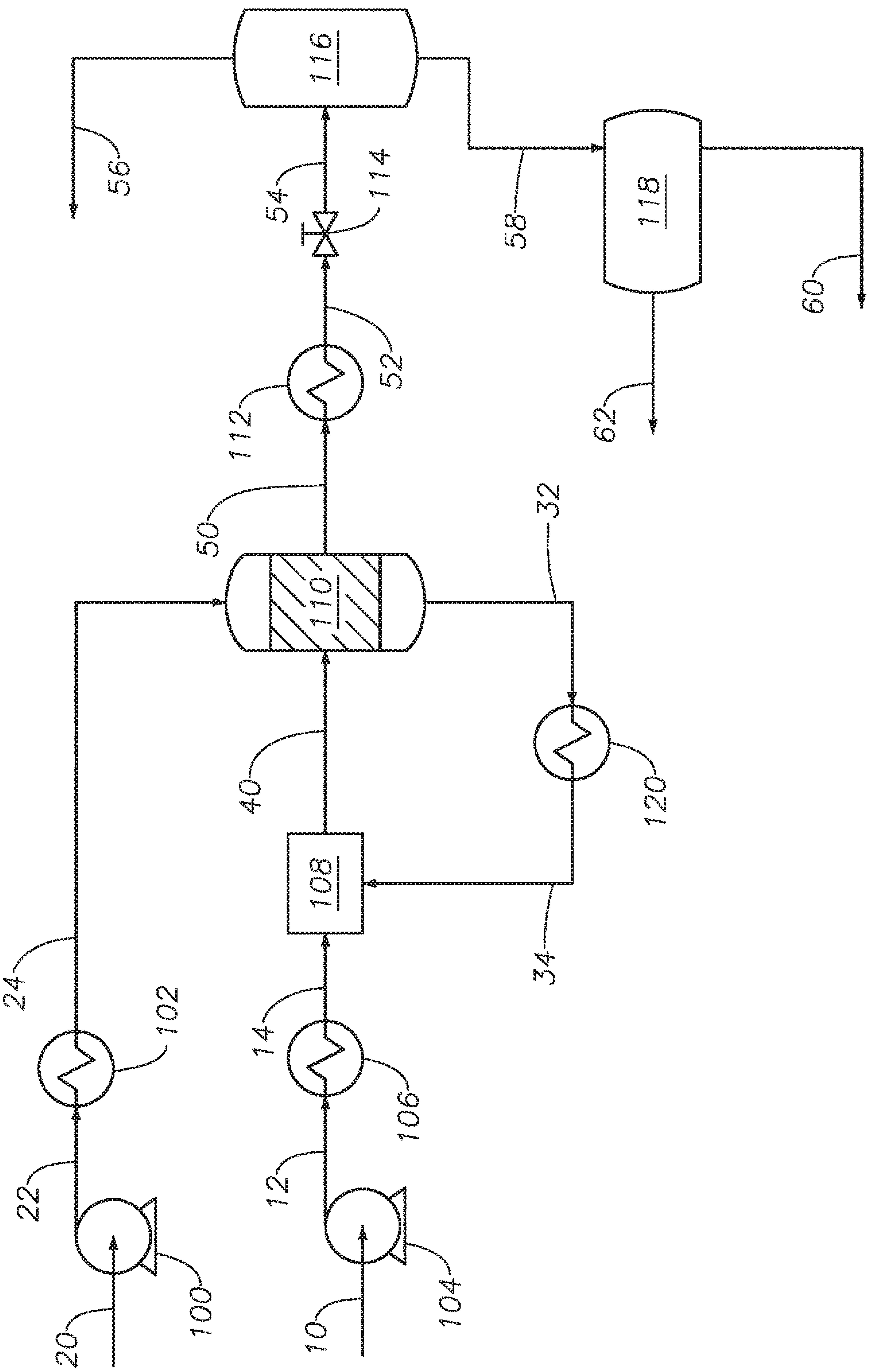
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FIG. 3

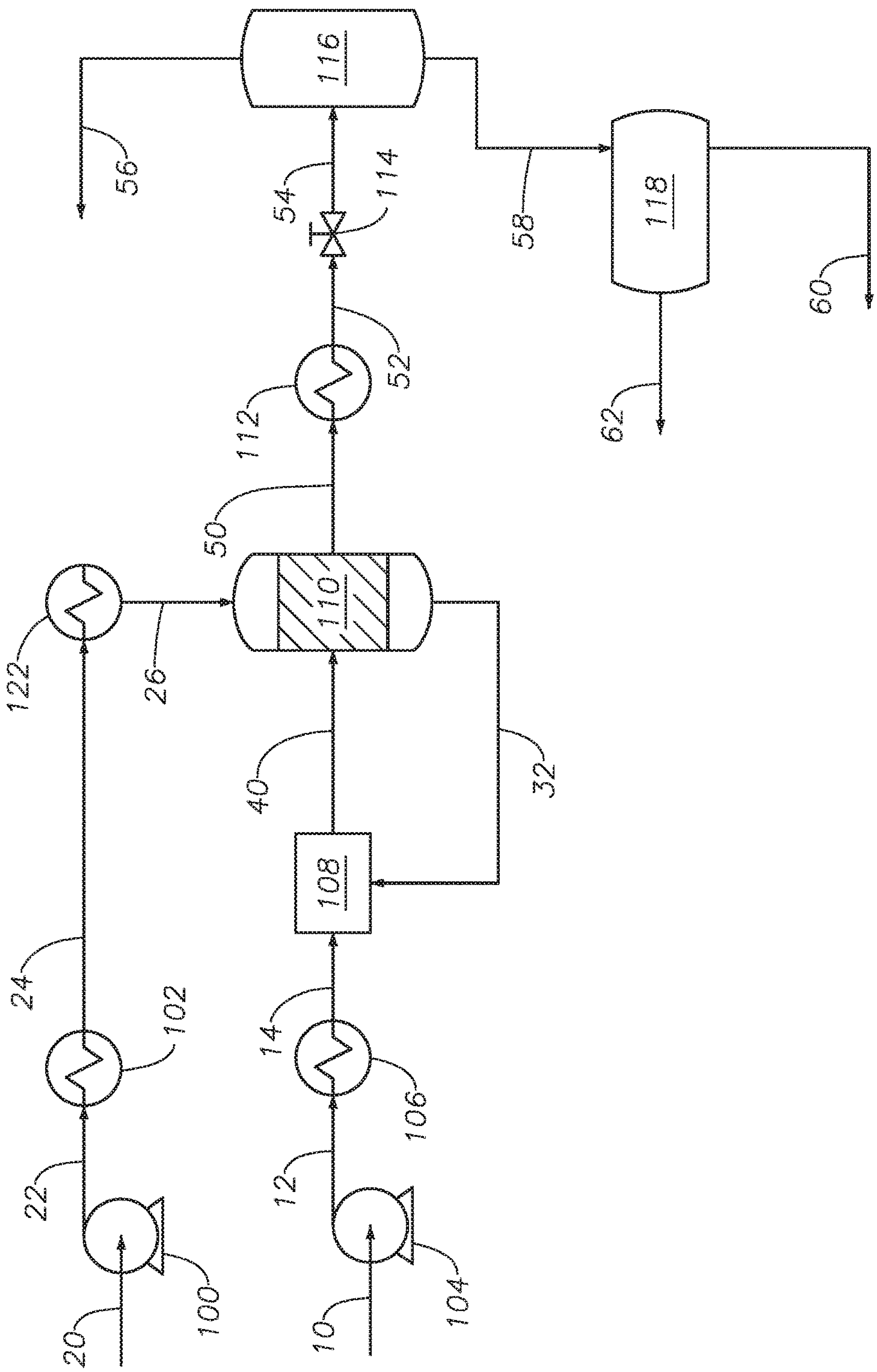
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FIG. 4

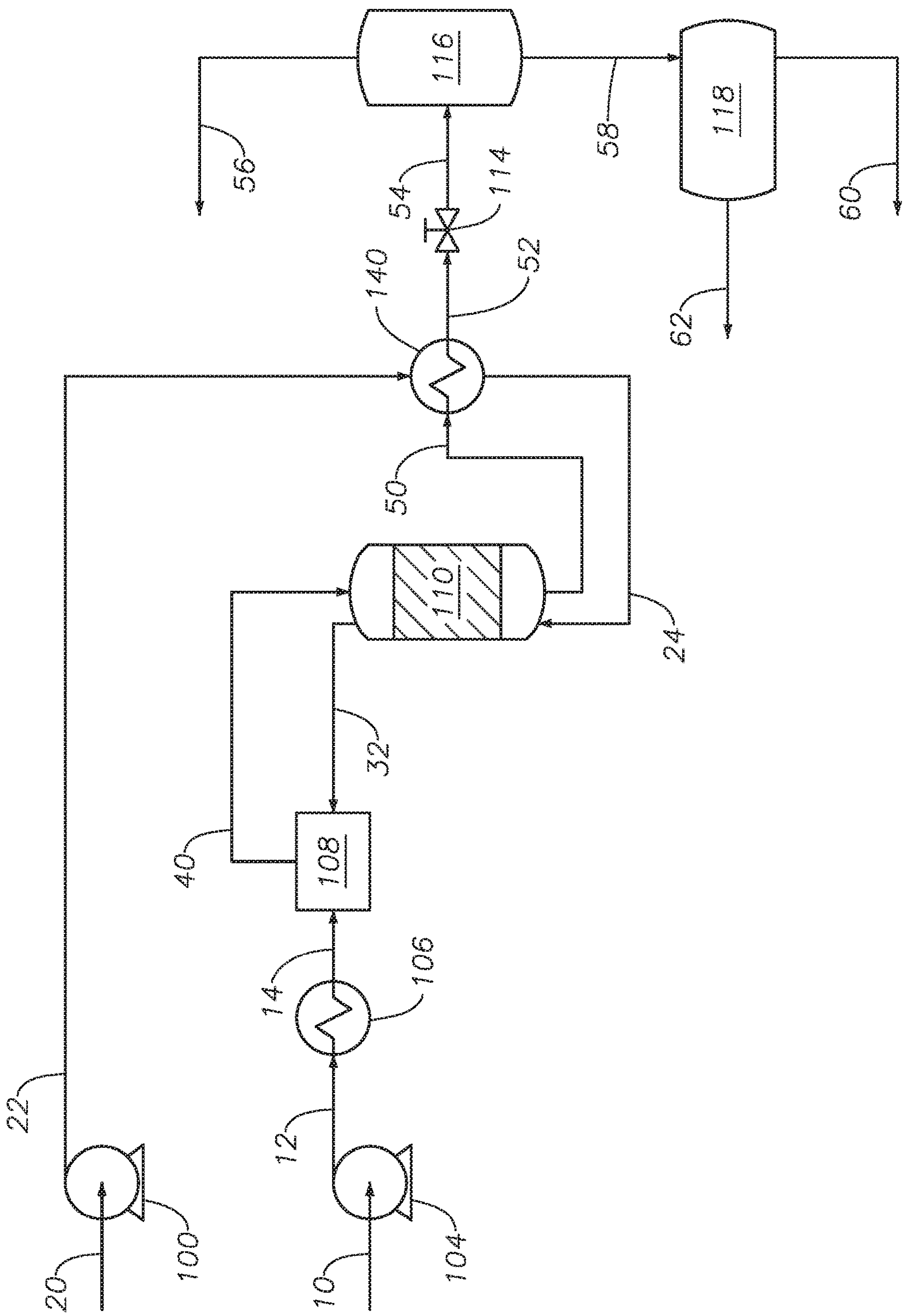
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FIG. 5

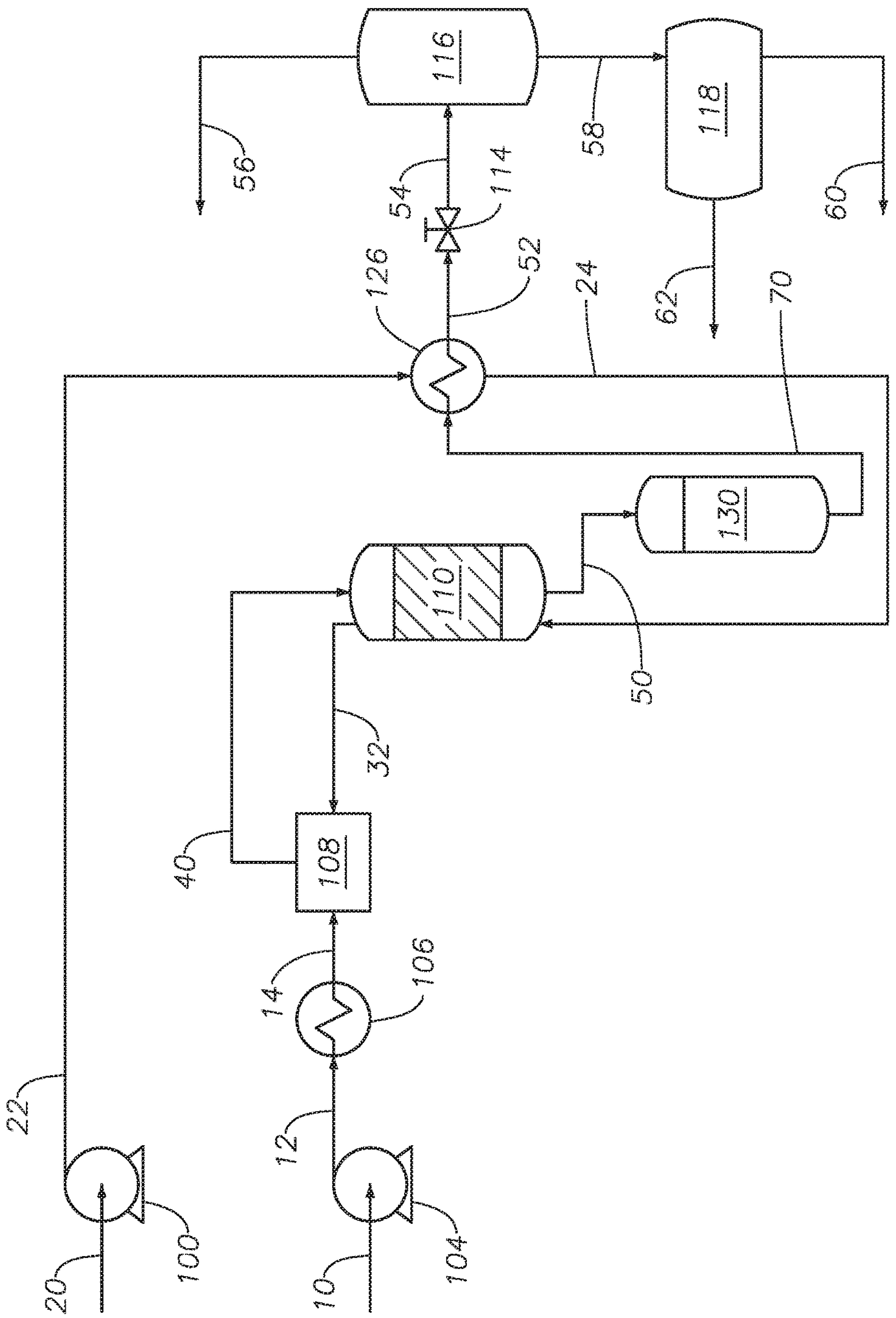
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FIG. 6

PROCESS FOR HEAVY OIL UPGRADING IN A DOUBLE-WALL REACTOR

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of and claims priority from U.S. Non-Provisional application Ser. No. 14/554,209 filed on Nov. 26, 2014. For purposes of United States patent practice, this application incorporates the contents of the Non-provisional Application by reference in its entirety.

TECHNICAL FIELD

This invention relates to a method and apparatus for reducing coke formation during upgrading of heavy oil. More specifically, the present invention relates to a method and apparatus for upgrading heavy oil in a double-wall reactor using supercritical water to reduce the formation of coke.

BACKGROUND

Increasing demand for gasoline and diesel requires more petroleum products of light and middle range distillates which can be mixed into gasoline and diesel pools. However, currently available hydrocarbon resources, most commonly include crude oil and other heavy fractions and heavy fraction distillates, requiring refining processes to generate desired products.

Conventional refining processes upgrade heavy oil into light and middle distillate range products with the aid of thermal energy, catalysts, and hydrogen. Representative conventional processes include catalytic hydroprocesses and coking processes. Catalytic hydroprocessing, such as hydrocracking, produces clean gasoline and diesel products, where impurities, such as sulfur, are minimized, but the premium quality of the products requires a huge consumption of hydrogen to produce. Coking processes, where catalysts and hydrogen are not employed, utilize thermal cracking reactions to upgrade heavy oil into gases, light distillates, and middle distillates, but also produce large amounts of low economic byproducts, such as solid coke.

A third option to upgrade heavy oil is the use of supercritical water. A low dielectric constant makes supercritical water a good solvent for organic compounds. Supercritical water has been used as a reaction medium for certain chemical reactions such as oxidation and for upgrading hydrocarbons. Supercritical water is a good reaction medium for upgrading because hydrogen can be transferred from the water to the hydrocarbons. Thus, a huge supply of hydrogen gas is not necessary. Supercritical water acts as a diluent, diluting the hydrocarbons. In upgrading heavy oil using supercritical water, as in thermal cracking, a radical is generated due to chemical bonds breaking. Molecular rearrangement follows radical propagation, including cracking, dimerization, and oligomerization. However, unlike in thermal cracking alone, upgrading reactions in supercritical water reduce the chance for radicals to be oligomerized, because the supercritical water acts as a "cage" to restrict the radicals. Radical species are stabilized by supercritical water through the cage effect (i.e., a condition whereby one or more water molecules surrounds the radical species, which then prevents the radical species from interacting). Stabilization of radical species is believed to help to prevent inter-radical condensation and thus, reduce the overall coke

production in the current invention. For example, coke production can be the result of the inter-radical condensation.

Coke, or petroleum coke, is a solid material formed in upgrading reactions. The solid material may leave the reactor with the liquid products, but commonly remains as a layer on the inner surfaces of the reactor and process piping. To be useful, coke requires further processing and is therefore considered a less valuable by-product to upgraded hydrocarbons.

Coking is a significant problem in upgrading reactions. Coking increases at increased temperatures. While the extent to which coking will occur is hard to predict, it is known that temperatures above 400° C. are enough to form coke. One reason coking is accelerated at higher temperatures is because radical formation is accelerated at higher temperatures. More radicals results in more oligomerization reactions, which increases the molecular condensation reactions or coke formation.

Hot spots contribute to coking in upgrading reactors. Hot spots occur due to localized heating of a metal surface, such as a reactor wall. In general, localized heating is caused by an irregular or non-uniform distribution of a direct heat source, such as a flame, an electric heater, a formation of an insulator on a metal surface, or an irregular fluid distribution on a metal surface. An example of an irregular fluid distribution on a metal surface would be the stoppage of process fluid flow in a tubular reactor. Thus, a furnace or heater must be designed for uniform distribution of temperature through the reactor walls. One design feature is to coat the surfaces of reactors with heat transfer materials to provide better heat distribution, but such heat transfer materials often have short life spans and are expensive to replace. A second design option is to ensure a high superficial velocity of the process fluid through the reactor. A high superficial velocity can improve temperature distribution. However, in some cases designing for high superficial velocity requires a high length to diameter ratio of the reactor tube which increases the cost of the reactor due to the material weight of the reactor tube. Any design should feature sensitive instrumentation for temperature monitoring throughout the reactor to prevent formation of hot spots. However, even with precise design and instrumentation, hot spots in a direct heating system are inevitable. At best, a reactor design can hope to minimize the number and intensity of hot spots.

Hot spots contribute to coking because they cause localized excessive heating of the fluid in the reactor. The excessive heating causes localized coke formation on the inner wall of the reactor. Once the coke forms on the inner wall both the size and intensity of the hot spot can increase leading to more coke formation. Additionally, the coke formation hinders accurate measurement of temperature in the reactor.

Coke formation during upgrading processes limits the functionality of the upgrading process. A reduction in the coke formed during upgrading would lead to an increased yield of liquid hydrocarbon products. Coke formation limits the run length, or residence time, the petroleum can spend in the reactor. Shorter residence times results in less efficient upgrading. Coke plugs the process lines causing an increase in the pressure of the process lines and the reactor. If the pressure increases above a certain point, the entire process must be shut down so the coke can be removed. Otherwise the pressure build-up could cause mechanical failure of the plant equipment. Coke formation is one of the common causes for unscheduled shut-downs of refining processes.

Supercritical water reduces coke formation compared to a purely thermal process. The extent of coking prevention by supercritical water, however, depends on the type of heavy oil. Even supercritical water is limited in preventing coke formation because molecules, especially, heavy molecules, are not easily dissolved in supercritical water due to their low solubility, so the larger molecules, such as asphaltenes, can be easily converted to coke through radical mediated reactions. Additionally, supercritical water at higher temperatures has lower density than heavy oil and that density changes more quickly as the temperature rises at supercritical pressures. At 25 MPa, the density of water at 400° C. is 166.54 kg/m^3 while at 450° C. the density is 108.98 kg/m^3. The relative difference in the density of heavy oil and supercritical water causes settling of heavy molecules on the reactor bottom or walls, where such segregated heavy molecules act as a precursor for coke formation. Even in supercritical water reactor, the aggregation of heavy molecules can lead to the formation of coke, and coke can lead to the formation of hot spots.

A supercritical water process that reduces or prevents the formation of hot spots would be advantageous. A supercritical water process that reduces the formation of coke and increases operational stability over conventional supercritical water processes would be advantageous.

SUMMARY

The current invention provides a process and apparatus for the upgrading of a hydrocarbon feedstock with supercritical water, wherein the upgrading process specifically excludes the use of a hydrothermal catalyst or the use of an external supply of hydrogen.

In a first aspect of the present invention, a process for reducing coke formation during hydrocarbon upgrading reactions using a double-wall reactor is provided. The process includes the steps of feeding a heated feed water to a shell-side volume of the double-wall reactor to produce a heat transfer stream. The double-wall reactor includes an exterior wall and an interior wall, the exterior wall and the interior wall defining the shell-side volume disposed between, a reaction section volume bounded by the interior wall, a heating element, the heating element adjacent to the exterior wall, wherein the heating element is configured to heat the heat transfer stream to create a hot water return, such that the heat transfer stream is above the critical temperature of water, wherein heat is transferred from the heat transfer stream through the interior wall to the reaction section volume, wherein the hot water return exits the shell-side volume, wherein the heat transfer stream is at a temperature greater than the critical temperature of water and is at a pressure greater than the critical pressure of water. The process further includes the steps of feeding the hot water return exiting the shell-side volume of the double-wall reactor through a filter, the filter is configured to remove particulates to form a filtered water stream, mixing the filtered water stream with a heated hydrocarbon feedstock in a mixer to produce a mixed stream, wherein the heated hydrocarbon feedstock is at a pressure greater than the critical pressure of water and at a temperature greater than 50° C., feeding the mixed stream to the reaction section volume of the double-wall reactor in a flow configuration counter-current to the heat transfer stream to create a reaction flow stream, reacting the reaction flow stream at a reaction temperature in the reaction section volume to produce a reactor effluent, wherein the heat transferred to the reaction section volume from the heat transfer stream is operable to maintain the reaction temperature above the critical temperature of water, cooling the reactor effluent in a reactor cooler to produce a cooled effluent, de-pressurizing the cooled effluent in a pressure reducer to produce a depressurized effluent, separating the depressurized effluent in a phase separator to produce a gas phase product and a liquid phase product, and separating the liquid phase product in a product separator to produce a separated water stream and an upgraded hydrocarbon stream.

In certain aspects of the present invention, the process further includes the step of recycling the separated water stream to combine with a feed water upstream of the double-wall reactor. In certain aspects of the present invention, the double-wall reactor further includes a shell-side inlet, the shell-side inlet configured to receive the heated feed water, a shell-side outlet, the shell-side outlet configured to eject the heat transfer stream as the hot water return, a reaction inlet, the reaction inlet configured to receive the mixed stream, and a reaction outlet, the reaction outlet configured to eject the reaction flow stream as the reactor effluent, wherein the shell-side inlet, the shell-side outlet, the reaction inlet, and the reaction outlet are configured to create the flow configuration counter-current between the heat transfer stream and the reaction flow stream. In certain aspects of the present invention, the double-wall reactor further includes baffles extending from the exterior wall into the shell-side volume, the baffles configured to increase heat transfer from the heating element and the exterior wall to the heat transfer stream. In certain aspects of the present invention, the process further includes the step of feeding the hot water return to a mixer pre-heater, the mixer pre-heater configured to increase the temperature of the hot water return to produce a hot mixer feed, and feeding the hot mixer feed to the filter to produce the filtered water stream. In certain aspects of the present invention, the process further includes the step of feeding the heated feed water to a water super heater, the water super heater configured to increase the temperature of the heated feed water to produce a hot water supply, and feeding the hot water supply to the shell-side volume of the double-wall reactor. In certain aspects of the present invention, the process further includes the steps of feeding the reactor effluent to a supercritical water reactor, the supercritical water reactor configured to upgrade hydrocarbons present in the reactor effluent, wherein the temperature of the supercritical water reactor is greater than the critical temperature of water, wherein the pressure of the supercritical water reactor is greater than the critical pressure of water, reacting the reactor effluent to produce a product stream, and feeding the product stream to the reactor cooler. In certain aspects of the present invention, liquid yield is greater than 98% by volume. In certain aspects of the present invention, the upgraded hydrocarbon stream has reduced amounts of asphaltene, sulfur, and other impurities. In certain aspects of the present invention, a residence time of the reaction flow stream in the double-wall reactor is greater than 10 seconds.

In a second aspect of the present invention, a supercritical water plant to upgrade hydrocarbons with reduced coke formation is provided. The supercritical water plant includes a hydrocarbon feedstock pump, the hydrocarbon feedstock pump configured to pressurize a hydrocarbon feedstock to a pressure above the critical pressure of water to produce a pressurized hydrocarbon feedstock, a hydrocarbon feedstock heater fluidly connected to the hydrocarbon feedstock pump, the hydrocarbon feedstock heater configured to heat the pressurized hydrocarbon feedstock to a temperature greater than 50° C. to produce a heated hydrocarbon feedstock, a feed water pump, the feed water pump configured to pressurize a feed water to a pressure above the critical pressure of water to produce a pressurized feed water, a feed water heater fluidly connected to the feed water pump, the feed water pump configured to heat the pressurized feed water to a temperature above the critical temperature of water to produce a heated feed water, a double-wall reactor, the double-wall reactor configured to upgrade the hydrocarbons with upgrading reactions, the double-wall reactor further configured to limit coke formation during the upgrading reactions. The double-wall reactor includes a shell-side inlet fluidly connected to the feed water heater, the shell-side inlet configured to receive the heated feed water to produce a heat transfer stream in a shell-side volume, an exterior wall and an interior wall, the exterior wall and the interior wall defining the shell-side volume disposed between, the shell-side volume configured to receive the heat transfer stream, a reaction section volume bounded by the interior wall, a shell-side outlet fluidly connected to the shell-side volume, the shell-side outlet configured to eject the heat transfer stream to produce a hot water return, and a heating element, the heating element adjacent to the exterior wall, wherein the heating element is configured to heat the heat transfer stream, such that the heat transfer stream is above the critical temperature of water, wherein heat is transferred from the heat transfer stream through the interior wall to the reaction section volume. The supercritical water plant further includes a filter fluidly connected to the shell-side outlet, the filter configured to remove particulates from the hot water return to form a filtered water stream, a mixer fluidly connected to the filter, the mixer configured to mix the filtered water stream and the heated hydrocarbon feedstock to produce a mixed stream, wherein the mixed stream is supplied to the reaction section volume of the double-wall reactor in a flow configuration counter-current to the heat transfer stream to produce a reaction flow stream, wherein the reaction section volume is operable to upgrade the hydrocarbons in the reaction flow stream to produce a reactor effluent, a reactor cooler fluidly connected to the double-wall reactor, the reactor cooler configured to cool the reactor effluent to a temperature below the critical temperature of water to produce a cooled effluent, a pressure reducer fluidly connected to the reactor cooler, the pressure reducer configured to reduce the pressure of the cooled effluent to a pressure below the critical pressure of water to produce a depressurized effluent, a phase separator fluidly connected to the pressure reducer, the phase separator configured to separate the depressurized effluent into a gas phase product and a liquid phase product, and a product separator fluidly connected to the phase separator, the product separator configured to separate the liquid phase product into an upgraded hydrocarbon stream and a separated water stream.

In certain aspects of the present invention, the separated water stream is combined with the feed water upstream of the feed water pump. In certain aspects of the present invention, the double-wall reactor further includes a reaction inlet, the reaction inlet configured to receive the mixed stream, and a reaction outlet, the reaction outlet configured to eject the reaction flow stream as the reactor effluent, wherein the shell-side inlet, the shell-side outlet, the reaction inlet, and the reaction outlet are configured to create the flow configuration counter-current between the heat transfer stream and the reaction flow stream. In certain aspects of the present invention, the double-wall reactor further includes baffles extending from the exterior wall into the shell-side volume, the baffles configured to increase heat transfer from the heating element and the exterior wall to the heat transfer stream. In certain aspects of the present invention, the supercritical water plant further includes a mixer pre-heater fluidly connected to the double-wall reactor, the mixer pre-heater configured to increase the temperature of the hot water return to produce a hot mixer feed, wherein the hot mixer feed is supplied to the filter to produce the filtered water stream. In certain aspects of the present invention, the supercritical water plant further includes a water super heater fluidly connected to the feed water heater, the water super heater configured to increase the temperature of the heated feed water to produce a hot water supply, wherein the hot water supply is supplied to the shell-side volume of the double-wall reactor. In certain aspects of the present invention, the supercritical water plant further includes a supercritical water reactor fluidly connected to the double-wall reactor, the supercritical water reactor configured to upgrade unreacted hydrocarbons present in the reactor effluent to produce a product stream, wherein the temperature of the supercritical water reactor is greater than the critical temperature of water, wherein the pressure of the supercritical water reactor is greater than the critical pressure of water, wherein the product stream is supplied to the reactor cooler. In certain aspects of the present invention, liquid yield is greater than 98% by volume. In certain aspects of the present invention, the upgraded hydrocarbon stream has reduced amounts of asphaltene, sulfur, and other impurities. In certain aspects of the present invention, a residence time of the reaction flow stream in the double-wall reactor is greater than 10 seconds.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following descriptions, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the invention and are therefore not to be considered limiting of the invention's scope as it can admit to other equally effective embodiments.

FIG. **1** provides a process diagram of one embodiment of the method of upgrading a hydrocarbon feedstock according to the present invention.

FIG. **2** provides a plan view of an embodiment of a double-wall reactor.

FIG. **2***a* provides a plan view of an embodiment of a double-wall reactor.

FIG. **3** provides a process diagram of one embodiment of the method of upgrading a hydrocarbon feedstock according to the present invention.

FIG. **4** provides a process diagram of one embodiment of the method of upgrading a hydrocarbon feedstock according to the present invention.

FIG. **5** provides a process diagram of one embodiment of the method of upgrading a hydrocarbon feedstock according to the present invention.

FIG. **6** provides a process diagram of one embodiment of the method of upgrading a hydrocarbon feedstock according to the present invention.

DETAILED DESCRIPTION

Although the following detailed description contains many specific details for purposes of illustration, it is understood that one of ordinary skill in the art will appreciate that many examples, variations and alterations to the following details are within the scope and spirit of the invention. Accordingly, the exemplary embodiments of the invention described herein and provided in the appended figures are set forth without any loss of generality, and without imposing limitations, relating to the claimed invention. Features of the embodiments can be combined with features of other embodiments.

Referring to FIG. **1**, an embodiment of a process for reducing coke formation in a double-wall reactor is provided. Hydrocarbon feedstock **10** is pressurized in hydrocarbon feedstock pump **104** to create pressurized hydrocarbon feedstock **12**. Hydrocarbon feedstock **10** can be from any hydrocarbon source. Exemplary hydrocarbon sources for use as hydrocarbon feedstock **10** include whole range crude oil, distilled crude oil, residue oil, vacuum residue oil, topped crude oil, bottom fraction of crude oil, product streams from oil refineries, vacuum gas oil, product streams from steam cracking processes, liquefied coals, liquid products recovered from oil or tar sands, bitumen, oil shale, asphaltene, biomass hydrocarbons, and the like. The pressure of pressurized hydrocarbon feedstock **12** is greater than about 22.064 MPa and alternately between about 22.1 MPa and about 31.9 MPa. In at least one embodiment of the present invention, the pressure of pressurized hydrocarbon feedstock **12** is 25.0 MPa. The critical pressure of water is 22.064 MPa.

Pressurized hydrocarbon feedstock **12** is heated in hydrocarbon feedstock heater **106** to form heated hydrocarbon feedstock **14**. The temperature of heated hydrocarbon feedstock **14** is between about 10° C. and about 300° C., alternately between about 50° C. and 250° C., alternately between about 50° C. and 200° C., alternately between about 50° C. and 150° C., alternately between about 50° C. and about 100° C., alternately between about 100° C. and about 200° C., alternately between about 150° C. and about 250° C., alternately between about 200° C. and about 300° C. In at least one embodiment of the present invention, the temperature of heated hydrocarbon feedstock **14** is greater than 50° C. In at least one embodiment of the present invention, the temperature of heated hydrocarbon feedstock **14** is 125° C. Hydrocarbon feedstock heater **106** can be any heat transfer unit capable of heating pressurized hydrocarbon feedstock **12**. Exemplary heat transfer units that can be employed as hydrocarbon feedstock heater **106** include natural gas fired heater, heat exchanger, and electric heater. In some embodiments, pressurized hydrocarbon feedstock **12** is heated in a cross-exchange operation in a heat exchanger with another process stream. In at least one embodiment of the present invention, hydrocarbon feedstock heater **106** is designed to minimize pressure drop such that the pressure of heated hydrocarbon feedstock **14** exiting hydrocarbon feedstock heater **106** is above the critical pressure of water. Heated hydrocarbon feedstock **14** is fed to mixer **108**.

Feed water **20** can be any source of water. In at least one embodiment, feed water **20** has a conductivity less than about 10.0 μmhos/cm. Conductivity is the most common way to determine the concentration of ionic compounds in the water. A higher conductivity indicates an increased presence of ionic compounds in the water. Ionic compounds such as sodium chloride can precipitate under supercritical water conditions, even though dissolved in water at subcritical conditions. Exemplary sources of water that can be utilized as feed water **20** include demineralized water, distillated water, boiler feed water, deionized water, and treated, recycled water. In at least one embodiment of the present invention, feed water **20** is a demineralized water. In at least one embodiment of the present invention, feed water **20** is in the absence of brine. In at least one embodiment of the present invention, feed water **20** includes water recycled from separated water stream **60**. Feed water **20** is pressurized in feed water pump **100** to produce pressurized feed water **22**. The pressure of pressurized feed water **22** is greater than about 22.064 MPa, alternately between about 22.1 MPa and about 31.9 MPa, alternately between about 22.9 MPa and about 31.1 MPa. In at least one embodiment of the present invention, the pressure of pressurized feed water **22** is 25.0 MPa. The critical pressure of water is 22.064 MPa.

Pressurized feed water **22** is heated in feed water heater **102** to create heated feed water **24**. The temperature of heated feed water **24** is greater than about 374° C., alternately between about 374° C. and about 600° C., alternately between 400° C. and about 550° C., alternately between about 400° C. and about 450° C., alternately between 450° C. and about 500° C., alternately between about 500° C. and about 550° C., alternately between about 550° C. and about 600° C. The maximum temperature of the water is selected in consideration of the materials of construction of the double-wall reactor **110** and the associated piping back to feed water heater **102**. In at least one embodiment of the present invention, the temperature of heated feed water **24** is 520° C. The critical temperature of water is 373.946° C. Feed water heater **102** can be any type of heat transfer unit capable of heating pressurized feed water **22**. Exemplary heat transfer units to employ as feed water heater **102** include a natural gas fired heater, a heat exchanger, an electric heater, or any heater or heat exchanger known in the art. In some embodiments of the present invention, pressurized feed water **22** is partially heated in a cross-exchange operation in a heat exchanger with another process stream of the process. Heated feed water **24** is supercritical water, above the critical temperature and the critical pressure, or critical point of water. Above the critical temperature and pressure, the liquid and gas phase boundary of water disappears, and the fluid has characteristics of both liquid and gaseous substances. Supercritical water is able to dissolve organic compounds like an organic solvent and has excellent diffusibility like a gas. Regulation of the temperature and pressure allows for continuous "tuning" of the properties of the supercritical water to be more liquid or more gas like. Supercritical water has reduced density and lower polarity, as compared to liquid-phase sub-critical water, thereby greatly extending the possible range of chemistry which can be carried out in water. Supercritical water has various unexpected properties as it reaches supercritical boundaries. Supercritical water has very high solubility toward organic compounds and has an infinite miscibility with gases. In certain embodiments, supercritical water generates hydrogen gas through a steam reforming reaction and water-gas shift reaction, which is then available for the upgrading reactions.

Heated feed water **24** is fed to double-wall reactor **110**. In at least one embodiment of the present invention, double-wall reactor **110** shares features with a double pipe heat exchanger. In at least one embodiment of the present invention, double-wall reactor **110** is designed to specification based on the process conditions, including flow rate. Double-wall reactor **110** is described with reference to FIG. **2**. Double-wall reactor **110** has exterior wall **210** and interior wall **212**. In at least one embodiment of the present invention, exterior wall **210** and interior wall **212** are formed of two concentric cylinders, open at both ends, the two concentric cylinders are not connected. In at least one embodiment of the present invention, double-wall reactor **110** is a double-pipe type vessel with an external heating source. The volume enclosed by interior wall **212** defines reaction section volume **214**. The volume between interior wall **212** and exterior wall **210** defines shell-side volume **216**. Reaction section volume **214** has one reaction inlet **230** and one reaction outlet **232**. Shell-side volume **216** has shell-side inlet **220** and shell-side outlet **222**. Heated feed water **24** enters shell-side volume **216** of double-wall reactor **110** through shell-side inlet **220** to create heat transfer stream **30**.

The design of double-wall reactor **110** that restricts exchange of fluids directly between shell-side volume **216** and reaction section volume **214** reduces the risk of mechanical failure (at joints, nozzles, ports, etc.), simplifies fabrication of double-wall reactor **110**, and provides for more manageable control of pressure and temperature. Temperature control in reaction section volume **214** and along interior wall **212** is an advantage of the present invention.

Heating element **218** is adjacent to exterior wall **210**. Heating element **218** is any direct heating source. Exemplary direct heating sources for use as heating element **218** include an electric heater, a gas fired heater, a liquid fired heater, and a coal fired heater. Heating element **218** transfers heat to heat transfer stream **30**. In at least one embodiment of the present invention, heating element **218** maintains the temperature of heat transfer stream **30** relative to the temperature of heated feed water **24**. In at least one embodiment of the present invention, heating element **218** extends the entire length or substantially the entire length of exterior wall **210**. In at least one embodiment of the present invention, heating element **218** extends for less than the entire length of exterior wall **210**. In at least one embodiment of the present invention, heating element **218** wraps around the entire circumference of exterior wall **210**. In at least one embodiment of the present invention, heating element **218** is adjacent to a portion of the circumference of exterior wall **210**. In at least one embodiment of the present invention, heating element **218** increases the temperature of heat transfer stream **30** above the temperature of heated feed water **24**. Heating of heat transfer stream **30** is in the absence of an oxidation reaction, which can contribute to run-away reaction temperatures. Heat is transferred from exterior wall **210** through heat transfer stream **30** in shell-side volume **216** to interior wall **212**, through interior wall **212** to reaction section volume **214**. The volume between interior wall **212** and exterior wall **210**, the flow rate of heat transfer stream **30**, and the temperature of heat transfer stream **30** are optimized in consideration of heat transfer requirements from exterior wall **210** through shell-side volume **216** to interior wall **212** and to improve the efficiency of heat transfer stream **30** as the heat transfer medium. The velocity of heat transfer stream **30** is influenced by the target reaction temperature.

In at least one embodiment of the present invention, the efficiency of heat transfer to heat transfer stream **30** can be improved by installing baffles **240** adjacent to exterior wall **210** and extending into shell-side volume **216**. Baffles **240** increase the heat transfer ability of heating element **218** to heat transfer stream **30** by increasing the surface area exposed to the flow of heat transfer stream **30**, creating a larger surface that interacts with heat transfer stream **30**. Improved heating of heat transfer stream **30** improves the efficiency of heat transfer from heat transfer stream **30** to reaction section volume **214**. In at least one embodiment of the present invention, baffles **240** are fins.

Double-wall reactor **110** is designed in consideration of optimizing the reactor parameters. Reactor parameters include residence time, reactor orientation, flow direction, reaction volume, reactor aspect ratio, and operating conditions. Residence time in double-wall reactor **110** is at least 5 seconds, alternately at least 10 seconds, alternately at least 15 seconds, alternately at least 20 seconds, alternately at least 30 seconds, and alternately at least 40 seconds. In at least one embodiment of the present invention, the residence time in double-wall reactor **110** is at least 10 seconds. Reactor orientation, as used herein, refers to how the reactor is aligned relative to ground. Exemplary reactor orientations include vertical and horizontal. In at least one embodiment of the present invention, double-wall reactor **110** has a vertical reactor orientation. Flow direction refers to whether the flow of mixed stream **40** is upflow or downflow in a vertical reactor orientation. In an upflow flow direction, reaction inlet **230** of double-wall reactor **110** is positioned nearer to grade relative to double-wall reactor **110** outlet and mixed stream **40** is fed to reaction inlet **230**. In a downflow flow direction, reaction inlet **230** is positioned farther from grade relative to reaction outlet **232**. Reaction volume refers to the total volume of reaction section volume **214**. The reaction volume is calculated in consideration of desired residence time, heat transfer efficiency of heated feed water **24**, and the reactor aspect ratio. Reactor aspect ratio is the ratio of the length to the diameter of double-wall reactor **110**. The aspect ratio plays a role in heat transfer capability, the residence time, and the flow regime. The operating conditions include reactor temperature and reactor pressure. Reactor temperature is defined as the temperature of the fluid at the end of reaction section volume **214**.

Referring again to FIG. **1**, heat transfer stream **30** exits shell-side volume **216** of double-wall reactor **110** as hot water return **32**. The temperature of hot water return **32** is within 10 degrees of the temperature of heated feed water **24**, alternately within 20 degrees, alternately within 30 degrees, alternately within 40 degrees, and alternately within 50 degrees. In at least one embodiment of the present invention, the temperature of hot water return **32** is above the temperature of heated feed water **24**. In at least one embodiment of the present invention, the temperature of hot water return **32** is below the temperature of heated feed water **24**. Hot water return **32** becomes one of the reactants in reaction section volume **214**.

Hot water return **32** flows through filter **124** to produce filtered water stream **36**. Filter **124** can be any type of filtering element known in the art that can remove particulates, including char. In at least one embodiment of the present invention, filter **124** has a metal housing. In at least one embodiment of the present invention, filter **124** includes a plurality of filtering elements arranged in a parallel assembly. Filtered water stream **36** is fed to mixer **108** to produce mixed stream **40**. In at least one embodiment of the present invention, hot water return **32** is in the absence of filter **124** and hot water return **32** mixes directly with heated hydrocarbon feedstock **14** in mixer **108**.

Filtered water stream **36** and heated hydrocarbon feedstock **14** are mixed externally from double-wall reactor **110**. Double-wall reactor **110** is in the absence of features designed to enhance mixing of reactants. Mixing heated hydrocarbon feedstock **14** and filtered water stream **36** in double-wall reactor **110** reduces the ability to maintain control of temperature, pressure, and flow-rate in double-wall reactor **110** creating unstable conditions in double-wall reactor **110**. Mixing heated hydrocarbon feedstock **14** and filtered water stream **36** upstream of double-wall reactor **110** (externally to double-wall reactor **110**) ensures a more uniform temperature profile of mixed stream **40** when entering double-wall reactor **110** and as it moves through reaction section volume **214** as reaction flow stream **42**, as shown in FIG. **2**. Mixer **108** can be any type of mixing device capable of mixing filtered water stream **36** and heated hydrocarbon feedstock **14**. In at least one embodiment of the present invention, mixer **108** is an inline mixer. Mixed stream **40** has a ratio of water to hydrocarbons represented by a ratio of the volumetric flow rate of feed water **20** (υ**20**) to the volumetric flow rate of hydrocarbon feedstock **10** ($\upsilon 10$). The ratio of $\upsilon 20$ to $\upsilon 10$ is in the range from about 10:1 to about 1:10 as measured at standard ambient temperature and pressure, alternately about 5:1 to about 1:5 as measured at standard ambient temperature and pressure, alternately less than 4:1 as measured at standard ambient temperature and pressure, alternately less than 3:1 as measured at standard ambient temperature and pressure, and alternately less than 2:1 as measured at standard ambient temperature and pressure. In at least one embodiment of the present invention, the ratio of $\upsilon 20$ to $\upsilon 10$ is 1.4:1 as measured at standard ambient temperature and pressure. In at least one embodiment of the present invention, the ratio of $\upsilon 20$ to $\upsilon 10$ is 2.5:1 as measured at standard ambient temperature and pressure. Mixed stream **40** is fed to reaction section volume **214** of double-wall reactor **110**. As used herein, "standard ambient temperature and pressure" refers to 25° C. and 0.1 MPa. Standard temperature and pressure refers to 0° C. and 0.1 MPa. Standard ambient temperature and pressure is more applicable.

Mixed stream **40** and heated feed water **24** are fed to double-wall reactor **110** in a counter-current flow configuration as illustrated in FIG. **2**. A counter-current flow configuration as used herein refers to the flow direction of the streams and means that the streams in double-wall reactor **110** enter the vessel from opposite ends, such that the feed location of one stream is adjacent to the exit location of a second stream. The counter-current flow configuration maintains uniform or substantially uniform temperature distribution in reaction flow stream **42** throughout the length of reaction section volume **214**. Reaction flow stream **42** receives heat through interior wall **212** via indirect heating from heat transfer stream **30** to maintain reaction flow stream **42** at the reaction temperature. Reaction flow stream **42** is continuous flow. Heat transfer stream **30** is continuous flow.

Double-wall reactor **110** is a supercritical reactor. Double-wall reactor **110** employs supercritical water as the reaction medium in reaction section volume **214** for hydrocarbon upgrading reactions in the absence of externally-provided hydrogen gas. Double-wall reactor **110** is in the absence of externally-provided oxidant. In at least one embodiment of the present invention, double-wall reactor **110** is in the absence of a catalyst. In at least one embodiment of the present invention, supercritical water acts as a diluent in double-wall reactor **110**. The structure of double-wall reactor **110** reduces the formation of coke by providing indirect heating to reaction section volume **214**. The absence of direct heating on interior wall **212** generates a uniform temperature distribution on interior wall **212**. The uniform temperature distribution reduces or eliminates the formation of hot spots on interior wall **212**. The reduction of hot spots reduces the formation of coke inside reaction section volume **214**. Exothermic and endothermic reactions affect the ability to control reaction temperature due to localized heating or cooling associated with the exothermic or endothermic reactions, respectively. Without being bound to a particular theory, it is believed that hydrocarbon fluid reactors that have non-uniform distribution of components and/or temperatures, also have non-uniform local temperature due to the exothermic or endothermic reactions. Double-wall reactor **110**, by producing a uniform temperature distribution, therefore reduces exothermic and/or endothermic reactions.

Reaction section volume **214** of double-wall reactor **110** produces reactor effluent **50**. In at least one embodiment of the present invention, the temperature of reactor effluent **50** is less than the reactor temperature due to cooling through the piping at the end of double-wall reactor **110** (not shown). In at least one embodiment of the present invention, the temperature of reactor effluent **50** is greater than the temperature of mixed stream **40** due to the indirect heating in double-wall reactor **110**. The reaction products in reactor effluent **50** are attributable to the composition of hydrocarbon feedstock **10**, the ratio of $\upsilon 20$ to $\upsilon 10$, and the operating temperature of reaction section volume **214** of double-wall reactor **110**.

Reactor effluent **50** is cooled in reactor cooler **112** to create cooled effluent **52**. Cooled effluent **52** has a temperature between about 10° C. and about 200° C., alternately between about 30° C. and about 120° C., alternately between about 50° C. and about 100° C. In at least one embodiment of the present invention, the temperature of cooled effluent **52** is 60° C. Reactor cooler **112** can be any heat transfer unit capable of cooling reactor effluent **50**. Exemplary heat transfer units that can be employed as reactor cooler **112** include heat exchangers, steam generators, cross-exchangers, or air coolers. According to at least one embodiment of the present invention as shown in FIG. **5**, reactor cooler **140** is a cross-exchanger that heats pressurized feed water **22** with heat from reactor effluent **50**, and in the process cools reactor effluent **50**. One of skill in the art will appreciate that cross-exchange heat exchangers can be utilized to provide energy recovery within the system.

The pressure of cooled effluent **52** is reduced in pressure reducer **114** to form depressurized effluent **54**. The pressure of depressurized effluent **54** is between about 0.11 MPa and about 2.2 MPa, alternately between about 0.05 MPa and about 1.2 MPa, alternately between about 0.05 MPa and about 1.0 MPa, alternately between about 0.11 MPa and about 0.5 MPa. In at least one embodiment of the present invention, the pressure of depressurized effluent **54** is 0.11 MPa. In at least one embodiment of the present invention, the pressure of depressurized effluent **54** is atmospheric pressure (101.3 kPa). Pressure reducer **114** can be any type of depressurizing device capable of reducing the pressure of cooled effluent **52**. Exemplary devices suitable for use as pressure reducer **114** include pressure control valve and capillary-type pressure let-down devices. Depressurized effluent **54** is fed to phase separator **116**.

Reactor effluent **50**, cooled effluent **52**, and depressurized effluent **54** contain water, upgraded hydrocarbons, and other hydrocarbons. Depressurized effluent **54** further includes gases, such as carbon dioxide. Reactor effluent **50**, cooled effluent **52**, and depressurized effluent **54** have a higher content of light hydrocarbons as compared to hydrocarbon feedstock **10**. The boiling point range of hydrocarbons in depressurized effluent **54** is lower compared to the boiling point range of hydrocarbons present in hydrocarbon feedstock **10**. A lower boiling point range of hydrocarbons indicates a lower content of heavy fraction hydrocarbons. The mass fraction of water present in reactor effluent **50**, cooled effluent **52**, and depressurized effluent **54** depends on the operating conditions in double-wall reactor **110**, the flow rate of feed water **20** and the feed ratio of water to hydrocarbon in mixed stream **40**.

Phase separator **116** separates depressurized effluent **54** into gas phase product **56** and liquid phase product **58**. Phase separator **116** is a gas-liquid separator. Exemplary separators for use as phase separator **116** include flash drum, flash column, multi-stage column, stripping-type column.

The operating conditions of reactor cooler **112**, pressure reducer **114**, and phase separator **116** are adjusted in consideration of the processing steps performed on gas phase product **56** and liquid phase product **58**. The operating conditions of reactor cooler **112**, pressure reducer **114**, and phase separator **116** influence the total amount and the compositions in gas phase product **56** and liquid phase product **58**.

Gas phase product **56** can be sent for further processing to recover components in the stream or alternately can be sent for processing and disposal. In at least one embodiment of the present invention, gas phase product **56** contains light hydrocarbon gases, including methane, ethane, ethylene, propane, and propylene. In at least one embodiment of the present invention, gas phase product **56** can be used as fuel gas. In at least one embodiment of the present invention, gas phase product **56** contains light hydrocarbon gases and hydrogen sulfide.

Liquid phase product **58** is fed to product separator **118** to separate liquid phase product **58** into upgraded hydrocarbon stream **62** and separated water stream **60**. Upgraded hydrocarbon stream **62** contains reduced impurities compared to hydrocarbon feedstock **10**. Upgraded hydrocarbon stream **62** can be sent for further processing, can be pooled with other upgraded hydrocarbons, or can be used in any other capacity appropriate for an upgraded hydrocarbon stream. The liquid yield of upgraded hydrocarbon stream **62** to hydrocarbon feedstock **10** was greater than 95%, alternately greater than 98%, alternately greater than 98.5%, and alternately greater than 99%. In at least one embodiment of the present invention, the liquid yield was greater than 98%. Liquid yield is a percentage of the total weight of upgraded hydrocarbon stream **62** divided by the total weight of hydrocarbon feedstock **10**. Liquid yield will be less than 100% because of loss of gases and water, wherein hydrocarbons are dissolved in water. Separated water stream **60** can be sent for further processing, can be stored onsite, can be sent for disposal, or can be recycled to the front of the process. In at least one embodiment of the present invention, separated water stream **60** is recycled to be mixed with or to be used as feed water **20**. Separated water stream **60** contains a total organic carbon content. The total organic carbon content is in the form of normal alkanes, aromatic compounds, and other hydrocarbons. Aromatic hydrocarbons have a higher solubility in supercritical water relative to normal alkanes. Removal of hydrocarbons from separated water stream **60** that is to recycled to the supercritical water process in double-wall reactor **110** is important to avoid the production of char due to hydrocarbon decomposition, which can plug the process lines. In at least one embodiment of the present invention, separated water stream **60** is treated to achieve a total organic carbon content of less than 20,000 ppm by weight, alternately less than 10,000 ppm by weight, alternately less than 5,000 ppm by weight, and alternately less than 1,000 by weight.

Process instrumentation and analyzers can be added to the system to improve the composition of upgraded hydrocarbon stream **62** by improving heating and pressure control of the process units.

Referring to FIG. **3**, an embodiment of the present invention is shown. According to the embodiment of the present invention as shown in FIG. **3** and with reference to FIG. **1** described herein, hot water return **32** exits shell-side volume **216** of double-wall reactor **110** and is fed to mixer pre-heater **120** to produce hot mixer feed **34**. Mixer pre-heater **120** can be any type of heat transfer unit capable of heating hot water return **32**. Exemplary heat transfer units for use as mixer pre-heater **120** include a natural gas fired heater, a heat exchanger, an electric heater, or any heater or heat exchanger known in the art. Hot mixer feed **34** is heated to a temperature above 374° C., alternately to a temperature above the temperature of hot water return **32** when it exits shell-side volume **216**, and alternately to a temperature between the temperature of hot water return **32** when it exits shell-side volume **216** and 600° C. In at least one embodiment of the present invention, mixer pre-heater **120** increases the temperature of hot water return **32**. Hot mixer feed **34** mixes with heated hydrocarbon feedstock **14** in mixer **108** to produce mixed stream **40**.

Referring to FIG. **4**, an embodiment of the present invention is shown. According to the embodiment of the present invention as shown in FIG. **4** and with reference to FIG. **1** described herein, heated feed water **24** exits feed water heater **102** and is introduced to water super heater **122** to produce hot water supply **26**. Water super heater **122** can be any type of heat transfer unit capable of heating heated feed water **24**. Exemplary heat transfer units for use as water super heater **122** include a natural gas fired heater, a heat exchanger, an electric heater, or any heater or heat exchanger known in the art. Hot water supply **26** is heated to a temperature above 374° C., alternately to a temperature above the temperature of heated feed water **24** when it exits feed water heater **102**, and alternately to the temperature between the temperature of heated feed water **24** when it exits feed water heater **102** and 600° C. In at least one embodiment of the present invention, water super heater **122**, increases the temperature of heated feed water **24**. Feed water heater **102** and water super heater **122** can be balanced for efficient heating to produce hot water supply **26**. Hot water supply **26** is fed to shell-side volume **216** of double-wall reactor **110**.

Referring to FIG. **6**, an embodiment of the present invention is shown. According to the embodiment of the present invention as shown in FIG. **6** and with reference to FIG. **1** described herein, pressurized feed water **22** is heated in feed water cross-exchanger **126** by cross exchanging with product stream **70**. Heating pressurized feed water **22** produces heated feed water **24** which is then fed to shell-side volume **216** of double-wall reactor **110** as described with reference to FIG. **1**. Reactor effluent **50** is fed to supercritical water reactor **130** downstream of double-wall reactor **110**.

Supercritical water reactor **130** is a supercritical reactor. Double-wall reactor **110** and supercritical water reactor **130** are in a two-reactor in series configuration. In a two-reactor in series configuration, the first reactor, double-wall reactor **110**, ensures mixing of hydrocarbons and supercritical water and upgrading reactions begin to occur. In the second reactor, supercritical water reactor **130**, the bulk of upgrading reactions occur, including cracking, desulfurization, and isomerization reactions. Ensuring the components are well-mixed in the first reactor eliminates all or substantially all of the hot spots in the second reactor. The elimination of hot spots prevents all or substantially all of the coke from forming in the second reactor. In at least one embodiment of the present invention, supercritical water reactor **130** is a single-wall reactor with a direct heating source. In at least one embodiment of the present invention, the second reactor is a double-wall reactor with a reaction section that is heated with indirect heating. In at least one embodiment of the present invention, the reactor parameters of double-wall reactor **110** and the reactor parameters of supercritical water reactor **130** are the same. In at least one embodiment of the present invention, the reactor parameters of double-wall reactor **110** and the reactor parameters of supercritical water reactor **130** are different. In at least one embodiment of the present invention, at least one of the reactor parameters of double-wall reactor **110** is the same as supercritical water reactor **130** and at least one of the reactor parameters of double-wall reactor **110** is different than supercritical water reactor **130**. Supercritical water reactor **130** produces product stream **70**. Product stream **70** is fed to feed water cross-exchanger **126**. Product stream **70** is cooled in feed water cross-exchanger **126** to produce cooled effluent **52**.

EXAMPLE

Comparative Example

Two simulations were created to compare a single-wall reactor and the double-wall reactor of the present invention.

In both simulations, a hydrocarbon feedstock at a rate of 10 barrels/day was pressurized to a pressure of 25.0 MPa and heated to a temperature of 125° C.

In the single-wall reactor simulation, the hydrocarbon feedstock was mixed with a feed water at a pressure of 25.0 MPa and a temperature of 460° C. The water stream was a water recycle stream from the liquid separator downstream of the reactor. The single-wall reactor was simulated as a tubular vessel having an internal volume of 10 L. The liquid yield was 95 wt %. Table 1 includes the operating conditions of the various streams. Table 2 shows the properties of the hydrocarbon feedstock and the upgraded hydrocarbon streams.

TABLE 1

Stream Operating Conditions

Stream Name	Hydrocarbon Feedstock	Water Feed	Heated Hydrocarbon Feedstock	Heated Water	Mixed Stream	Reactor Effluent	Cooled Effluent	Depressurized Stream
Temp (° C.)	25	25	125	460	365	450	50	45
Pressure (MPa)	0.11	0.11	25.0	25.0	25.0	24.8	24.6	0.11

TABLE 2

Stream Properties

Properties	Hydro-carbon Feedstock	Upgraded Hydrocarbon Stream
Specific Gravity (API)	17	24
Asphaltene (wt %)	13.0	2.0
Sulfur (wt % S)	3.2	2.6

In the double-wall reactor simulation, the embodiment was simulated as described with reference to FIG. **1**. Feed water **20** was pressurized to a pressure of 25.0 MPa and heated to a temperature of 450° C. and then fed to shell-side volume **216** of double-wall reactor **110** as heated feed water **24**. Hot water return **32** exiting double-wall reactor **110** was mixed with heated hydrocarbon feedstock **14** and fed to reaction section volume **214** of double-wall reactor **110** in a counter-current flow configuration to heated feed water **24**. Feed water **20** was recycled from product separator **118** as at least a fraction of separated water stream **60**. The temperature of hot water return **32** was 480° C. due to heating element **218** on exterior wall **210** of double-wall reactor **110**. In the simulation, heating element **218** was simulated as an external gas fired heater. Liquid yield was 98 wt %. The operating conditions are in Table 3. The stream properties are in Table 4.

TABLE 3

Stream Operating Conditions

Stream Name	Hydrocarbon Feedstock 10	Feed Water 20	Heated Hydrocarbon Feedstock 14	Heated Feed Water 24	Mixed Stream 40	Reactor Effluent 50	Cooled Effluent 52	Depressurized Effluent 54
Temp (° C.)	25	25	125	450	373	430	50	50
Pressure (MPa)	0.11	0.11	25.0	25.0	25.0	25.0	24.8	0.11

TABLE 4

Stream Properties

Properties	Hydro-carbon Feedstock	Upgraded Hydrocarbon Stream
Specific Gravity (API)	17	25
Asphaltene (wt %)	13.0	1.8
Sulfur (wt % S)	3.2	2.5

Without being bound to any particular theory, it is believed that the absence of hot spots in the double-wall reactor as compared to the single-wall reactor resulted in the higher liquid yield, 98 wt % for the double-wall reactor vs. 95 wt % for the single-wall reactor, and better quality product, lower asphaltene weight percent and sulfur weight percent, even at lower reactor temperature, 430° C. for the double-wall reactor vs. 450° C. for the single-wall reactor. It is suspected that hot spots in the single-wall reactor simulation induced condensation reactions between heavy molecules, which caused coke formation, as well as over-cracking to produce gas phase product. Condensation reaction traps sulfur and metals in the heavier molecules that are products of condensation reactions.

Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations can be made hereupon without departing from the principle and scope of the invention. Accordingly, the scope of the present invention should be determined by the following claims and their appropriate legal equivalents.

The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

Optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

Ranges may be expressed herein as from about one particular value, and/or to about another particular value.

When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within said range.

That which is claimed is:

1. A supercritical water plant to upgrade hydrocarbons with reduced coke formation, the supercritical water plant comprising:

a hydrocarbon feedstock pump, the hydrocarbon feedstock pump configured to pressurize a hydrocarbon feedstock to a pressure above the critical pressure of water to produce a pressurized hydrocarbon feedstock;

a hydrocarbon feedstock heater fluidly connected to the hydrocarbon feedstock pump, the hydrocarbon feedstock heater configured to heat the pressurized hydrocarbon feedstock to a temperature greater than 50° C. to produce a heated hydrocarbon feedstock;

a feed water pump, the feed water pump configured to pressurize a feed water to a pressure above the critical pressure of water to produce a pressurized feed water;

a feed water heater fluidly connected to the feed water pump, the feed water pump configured to heat the pressurized feed water to a temperature above the critical temperature of water to produce a heated feed water;

a double-wall reactor, the double-wall reactor configured to upgrade the hydrocarbons with upgrading reactions, the double-wall reactor further configured to limit coke formation during the upgrading reactions, the double-wall reactor comprising:

a shell-side inlet fluidly connected to the feed water heater, the shell-side inlet configured to receive the heated feed water to produce a heat transfer stream in a shell-side volume;

an exterior wall and an interior wall, the exterior wall and the interior wall defining the shell-side volume disposed between, the shell-side volume configured to receive the heat transfer stream;

a reaction section volume bounded by the interior wall;

a shell-side outlet fluidly connected to the shell-side volume, the shell-side outlet configured to eject the heat transfer stream to produce a hot water return; and

a heating element, the heating element adjacent to the exterior wall, wherein the heating element is configured to heat the heat transfer stream, such that the heat transfer stream is above the critical temperature of water, wherein heat is transferred from the heat transfer stream through the interior wall to the reaction section volume;

a filter fluidly connected to the shell-side outlet, the filter configured to remove particulates from the hot water return to form a filtered water stream;

a mixer fluidly connected to the filter, the mixer configured to mix the filtered water stream and the heated hydrocarbon feedstock to produce a mixed stream, wherein the mixed stream is supplied to the reaction section volume of the double-wall reactor in a flow configuration counter-current to the heat transfer stream to produce a reaction flow stream, wherein the reaction section volume is operable to upgrade the hydrocarbons in the reaction flow stream to produce a reactor effluent;

a reactor cooler fluidly connected to the double-wall reactor, the reactor cooler configured to cool the reactor effluent to a temperature below the critical temperature of water to produce a cooled effluent;

a pressure reducer fluidly connected to the reactor cooler, the pressure reducer configured to reduce the pressure of the cooled effluent to a pressure below the critical pressure of water to produce a depressurized effluent;

a phase separator fluidly connected to the pressure reducer, the phase separator configured to separate the depressurized effluent into a gas phase product and a liquid phase product; and

a product separator fluidly connected to the phase separator, the product separator configured to separate the liquid phase product into an upgraded hydrocarbon stream and a separated water stream.

2. The supercritical water plant of claim 1, wherein the separated water stream is combined with the feed water upstream of the feed water pump.

3. The supercritical water plant of claim 1, wherein the double-wall reactor further comprises:

a reaction inlet, the reaction inlet configured to receive the mixed stream; and

a reaction outlet, the reaction outlet configured to eject the reaction flow stream as the reactor effluent,

wherein the shell-side inlet, the shell-side outlet, the reaction inlet, and the reaction outlet are configured to create the flow configuration counter-current between the heat transfer stream and the reaction flow stream.

4. The supercritical water plant of claim 1, wherein the double-wall reactor further comprises:

baffles extending from the exterior wall into the shell-side volume, the baffles configured to increase heat transfer from the heating element and the exterior wall to the heat transfer stream.

5. The supercritical water plant of claim 1, further comprising:

a mixer pre-heater fluidly connected to the double-wall reactor, the mixer pre-heater configured to increase the temperature of the hot water return to produce a hot mixer feed, wherein the hot mixer feed is supplied to the filter to produce the filtered water stream.

6. The supercritical water plant of claim 1, further comprising:

a water super heater fluidly connected to the feed water heater, the water super heater configured to increase the temperature of the heated feed water to produce a hot water supply, wherein the hot water supply is supplied to the shell-side volume of the double-wall reactor.

7. The supercritical water plant of claim 1, further comprising:

a supercritical water reactor fluidly connected to the double-wall reactor, the supercritical water reactor configured to upgrade unreacted hydrocarbons present in the reactor effluent to produce a product stream, wherein the temperature of the supercritical water reactor is greater than the critical temperature of water, wherein the pressure of the supercritical water reactor is greater than the critical pressure of water,

wherein the product stream is supplied to the reactor cooler.

8. The supercritical water plant of claim 1, wherein a liquid yield of the upgraded hydrocarbon is greater than 98% by volume.

9. The supercritical water plant of claim 1, wherein the upgraded hydrocarbon stream has reduced amounts of asphaltene, sulfur, and other impurities relative to the hydrocarbon feedstock.

10. The supercritical water plant of claim **1**, wherein a residence time of the reaction flow stream in the double-wall reactor is greater than 10 seconds.

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